# Influence of Sodium Loading on CO Adsorption over Faujasite Zeolite Supported Gold Monomers: a Density Functional Study

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*Abstract*

The interaction of carbon monoxide with the gold monomer in two oxidation states 0 and +1 both in the gas phase and on an NaY zeolite support is studied using density functional theory (DFT).Three structures of the zeolite having different Na ion loading are considered.CO vibrational frequency shows a blue shift on going from the oxidation state 0 to +1.The CO binding energy values of 1.19 and 1.21 eV for the oxidation state 0 are higher than the corresponding values in the oxidation state +1.This is irrespective of the number of Na ions present in the cluster.

*Keywords*

*NaY Zeolite; Gold Monomer; CO Adsorption; Density Functional Theory*

## Introduction

The high surface-to-volume ratio in metal clusters provides a large number of low coordinated atoms which can serve as active sites in catalysis.Among the metal clusters, gold has attracted the attention of a large number of researchers due to their applications as catalysts in several reactions including CO oxidation.A lot of studies, both theoretical and experimental, have been undertaken to determine the structural and electronic properties of clusters in the gas phase as well as on support and to examine their interaction with adsorbates. The factors determining the catalytic activity of the nanocluster are size, structure and charge state of the cluster, nature of the support and the cluster support interaction. Phala et al. studied the chemisorption of hydrogen and carbon monoxide onto small gold clusters $Au_n$ (n=1-13) using density functional theory. Zhai and Wang made a photoelectron spectroscopy (PES) study of CO adsorbed gold clusters $Au_mCO_n^-$(m=2-5, n=0-7).They found that adsorption of the first few CO leads to significant shifts in the PES spectra compared to the

bare cluster indicating strong chemisorptions of CO on the gold cluster.Additional CO then physisorb onto the chemisorption saturated gold clusters. Sun et al. investigated the chemisorption of $O_2$ on gold cluster anions $Au_n^-$, n=2,4,6 at room temperature, both theoretically and experimentally.Yoon et al. determined that the $Au_8$ cluster bound to an oxygen-vacancy F-centre defect of MgO(001) is the smallest cluster that can catalyse the oxidation of CO to $CO_2$ at temperatures as low as 140 K.The metal carbonyl bond is attributed to a balance between two processes, namely, electron donation from a filled σ orbital of the CO to an empty symmetry compatible metal orbital and back donation from filled d-type metal orbitals to empty $\pi^*$ orbitals of the CO.

Zeolites with adjustable acidic properties having pores and cavities of molecular dimensions form an important class of support for nanoclusters in catalysis. The charged state of the cluster depends upon the concentration of the acidic centres in the zeolite which can be modified. This renders it possible to study the effect of varying charge of the cluster on catalytic properties. Fierro-Gonzalez and Gates, who synthesized and characterized mononuclear $Au^I$ and $Au^{III}$ complexes in zeolite NaY, found that under the condition of CO oxidation catalysis at 298 K and 760 Torr the gold remained mononuclear and that the $Au^{III}$ complex is more active as a catalyst compared to the $Au^I$ complex. Simakov et al. investigated the influence of Na substitution on oxidation of CO in Y zeolites and found two types of active sites, viz, partly charged gold clusters $Au_n^{\delta+}$ for low temperature activity and gold nanoparticles $Au_m^0$ for high temperature activity. It is thus seen that the oxidation state of the zeolite supported cluster greatly influences its catalytic activity.

In an earlier study we had investigated the adsorption of the CO molecule on the gold monomer in three oxidation states 0, +1 and +3 both in the gas phase and on a 9T cluster of faujasite zeolite support using density functional theory. In this paper, we investigate the modification of the 9T cluster of faujasite zeolite support by replacing the compensating protons with sodium cations one at a time, and its effect on CO adsorption.

The oxidation state of gold nanoclusters greatly influences their catalytic activity. The findings of our study of CO adsorption on NaY zeolite supported gold monomer in two most common oxidation states will provide guidelines for studies on CO oxidation. We have considered three kinds of faujasite zeolite support having different sodium ion contents.The results obtained from this work will enable a comparison between gold monocarbonyls on zeolite support with different sodium ion contents.

## Computational Details

In faujasite zeolite, the catalytically active extra-framework cations are located at three main crystallographic sites, viz. site I, II and III. (Fig. 1) Site I cations are located in the hexagonal prisms, which connect sodalite cages.Site II cations are in the supercage, coordinating with three oxygen atoms of the 6-ring window of the sodalite cage. Cations in site III are located in the four-ring window. Site II is considered for our investigations. The framework of zeolite has been modelled with a T9 (T=tetrahedral unit of zeolite) cluster containing a six-member ring and three other Si atoms of the wall of the supercage which is accessible by metal clusters and adsorbed molecules.  Three Si atoms of the six-member ring were isomorphously substituted by three Al atoms in an alternating sequence according to the Löwenstein rule.Thus the Si/Al ratio for our cluster is 2.The excess negative charges generated due to three Al atoms were compensated by protons and sodium cations, or sodium cations alone.The charge on the adsorbed gold atom was varied by changing the number of compensating charges.Three compensating charges made the adsorbed gold atom neutral, while two compensating charges meant that the adsorbed gold atom carried a charge of +1.The free valences of silicon and aluminum atoms were saturated with hydrogen atoms.

At first, only Si—H, Al—H and O—H bonds were optimized keeping the position of other atoms fixed at their crystallographic positions In subsequent calculations, the optimized positions of the terminating hydrogen atoms were held fixed and all other atoms were allowed to relax.
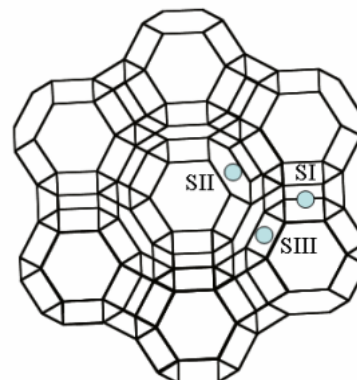


FIG. 1 POSITION OF EXTRA-FRAMEWORK CATIONS IN FAUJASITE ZEOLITES

All the calculations have been performed with DMol³ program  by using the DNP basis set.The DNP basis functions are the double-numerical atomic orbitals augmented by polarization functions, i.e, functions with angular momentum one higher than that of the highest occupied orbital in the free atom.  Gold being a heavy atom, relativistic effects become important.So, all-electron calculations with scalar relativistic corrections (VPSR) have been used.Our choice of exchange correlation functional was guided by the fact that LDA functionals give a better description of geometry and GGA functionals are better suited to describe molecular properties in case of zeolite supported metal clusters.So for both gas phase and supported clusters, geometry optimizations and frequency calculations were performed by using the VWN functional.In an earlier investigation on the geometrical and electronic properties of gold clusters, it has been determined that among the available GGA functionals, BLYP, which incorporates Beckes's exchange  and Lee-Yang-Parr correlation, gives the best estimate of molecular properties of the gold dimer. Therefore, single point calculations were carried out at the VWN optimized geometry with the GGA functional BLYP, in order to determine energy and other properties. In the results to follow, the binding energies are computed as

$$E_B(CO) = - [E_{AuCO} - E_{Au} - E_{CO}] \text{ in gas phase} \qquad (1)$$

$$E_B(Au^{0,+}) = - [E_{zeolite-Au\ complex} - E_{Au}^{0,+} - E_{zeolite}]$$
$$\text{for the Au-zeolite complex} \quad (2)$$

$$E_{B-zeo}(CO) = - [E_{zeolite-Au-CO\ complex} - E_{zeolite-Au\ complex} - E_{CO}]$$
$$\text{for the Au-zeolite-CO complex} \quad (3)$$

In all cases, positive values correspond to exothermic processes.

## Results and Discussion

### *Adsorption of CO on gas phase gold atom*

All electron scalar-relativistic calculations have been performed without using any symmetry constraint to study the adsorption of the CO molecule onto the gold monomer in various oxidation states. The optimized structures are given in Fig. 2.
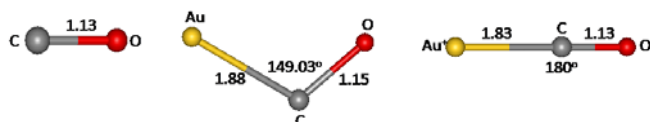


FIG. 2. OPTIMIZED STRUCTURE OF  CO ADSORBED Au ATOM IN THE GAS PHASE. BOND LENGTHS ARE IN ANGSTROMS (Å) AND BOND ANGLE IS IN DEGREE

Our optimized geometry of the CO molecule gives a bond length of 1.133 Å, which compares well with the experimental value of 1.128 Å Our calculations for CO adsorbed on the neutral Au atom reveal a strongly bound molecule (0.88 eV) with a shift of -128.9 $cm^{-1}$ in the CO vibrational frequency, computed as the difference between the harmonic frequency of AuCO and the free CO molecule.The structure is a bent one with the Au-C-O angle of $149^0$. The CO bond length elongates to 1.151 Å in keeping with the red shift in the CO vibrational frequency.The Au-C bond length is 1.88 Å.Giordano et al. obtained values of the Au-C-O bond angle between $139^0$ and $142^0$  and vibrational shift between -125 and -162 $cm^{-1}$ by DFT method using various functionals. Moving over to the  gold monomer in the oxidation state +1, the adsorption of CO leads to a linear molecule with the CO binding energy value of 2.54 eV. The properties of the adsorption complexes are listed in Table 1.

TABLE 1. COMPUTATIONAL RESULTS OF CO ADSORPTION OF GOLD ATOM IN THE GAS PHASE. BOND LENGTHS ARE IN ANGSTROMS (Å) AND BOND ANGLE IS IN DEGREE.

| System | Bond Length (Å) | | B. E. (eV) | $\omega_e$(CO) ($cm^{-1}$) | $\Delta\omega$ ($cm^{-1}$) | $\alpha$ ($^0$) |
|---|---|---|---|---|---|---|
| | C-O | Au-C | | | | |
| CO | 1.133 | | | 2179.8 | | |
| AuCO | 1.15 | 1.88 | 0.88 | 2050.9 | -128.9 | 149.03 |
| Au$^+$CO | 1.13 | 1.83 | 2.54 | 2263.5 | 83.7 | 180.00 |

Wu et al. found that the binding energy of CO on monomeric gold increases on going from anionic to neutral, and then from neutral to cationic species. They concluded that CO → metal electron donation is the dominant mechanism in the formation of the metal-CO bond. In our case as well, it has been found that the binding energy of the CO molecule increases with increment of positive charge on the gold atom (Table 1). That is, as the atom becomes more and more deficient in electrons, the interaction with the CO molecule becomes stronger. From Table 1, it is observed that the vibrational frequency of the CO molecule in Au$^+$CO is higher than the frequency of free CO. While there are several factors responsible for this shift in the CO vibrational frequency, one plausible explanation may be given from the electron donation/back-donation mechanism. The molecular orbitals of the CO molecule interacting with the metal are the 5σ (the HOMO), which is weakly antibonding and 2π* (the LUMO), which is highly antibonding. While interacting with positively charged metal centers, CO acts as a Lewis base. The filled 5σ orbital donates electrons to the empty metal orbitals. This shifts the CO vibrational frequency to higher values. Our obtained CO vibrational frequency of 2263.5 $cm^{-1}$ presents a blue shift of 83.7 $cm^{-1}$, which is fairly in agreement with the experimental blue shift of 93.8 $cm^{-1}$, obtained by laser ablation techniques.

### *Adsorption of CO on NaY zeolite supported gold atom*

All electron scalar-relativistic calculations have been performed without using any symmetry constraint to study the adsorption of CO molecule onto the zeolite supported gold monomer in various oxidation states.All calculations were spin-restricted for closed shell systems and spin-unrestricted for open shell systems. The optimized structures of the neutral gold atom supported on the six-member ring of faujasite zeolite containing one, two and three sodium cations are shown in Fig. 3, structures  (a), (b) and (c) of which show the zeolite supported neutral gold atoms without CO, while (d), (e) and (f) show the opmized geometries of the supported gold monomer with adsorbed CO.Table 2 lists the geometric and electronic properties of the adsorption complexes.

The complex Au-FAU-Na1 is formed by adsorbing a neutral gold atom on a 9T cluster of faujasite zeolite in which the excess negative charges generated due to substitution of three silicon atoms by aluminium atoms are compensated by two protons and a sodium cation. In Au-FAU-Na2 and Au-FAU-Na3, two sodium cations and a proton, and three sodium cations, respectively, are used for charge compensation. The optimized geometries are shown in Figs. 3 and 4 for the NaY zeolite supported gold atom in the oxidation states 0 and +1, respectively. The effect of the increasing sodium cation content on the

electronic and structural properties of the supported gold monomer is being investigated. It is observed from Table 2 that the Au—O distances show a decreasing trend on going to higher oxidation states. This is irrespective of the sodium ion content.The Au—O distances for the neutral gold monomer with one, two and three sodium cations are found to be 2.36, 2.30 and 2.52 Å, respectively, while those for the oxidation state +1 are 2.17 and 2.15 Å, respectively for one and two sodium cations
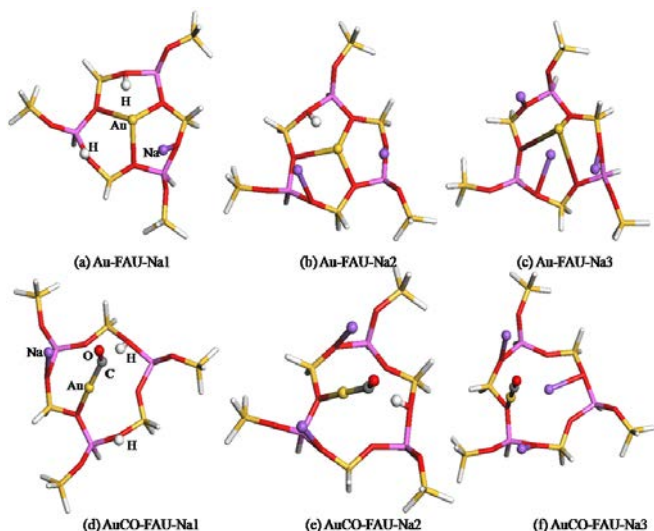


FIGS. 3. OPTIMIZED STRUCTURES OF (a-c) GOLD ATOM (Au⁰) AND (d-f) AND GOLD CARBONYLS ADSORBED ON THE SIX MEMBER RING OF NaY ZEOLITE.

The carbonyl complexes were formed by adsorbing a CO molecule on the supported Au monomer. Structures containing one and two sodium cations were found to retain their gas phase structures respectively, with only a slight decrease in the Au-C-O bond angle, while the structure containing three sodium cations exhibited a large increase in the Au-C-O bond angle compared to the gas phase value. The C-O bond length of the supported gold carbonyl was found to vary from 1.14 to 1.19 Å which is only slightly higher than the gas phase value of 1.13 Å. A comparison of the structures of the zeolite supported gold monomers with and without CO shows that for both the oxidation states Au-O bond distances decrease on CO adsorption, indicating that CO facilitates stronger interaction of the Au atom with the support. The Au-O bond lengths in the supported carbonyls are 2.10, 2.09 and 2.04 Å, respectively in the oxidation state 0. The corresponding values in oxidation state +1 are 2.05 and 2.06 Å, respectively. The change in Au-O bond length is larger in case of Au⁰. It is also observed from Table 2 that the Au-O bond distance decreases on going to the higher

oxidation state of the gold atom.Thus the gold carbonyl in the oxidation state +1 is more strongly anchored to the zeolite support.The Au-Al bond distances in the carbolyls are 3.29, 3.16 and 3.09 Å for CO adsorbed on the gold monomer in the oxidation states 0 when the structure contains one, two and three sodium cations,
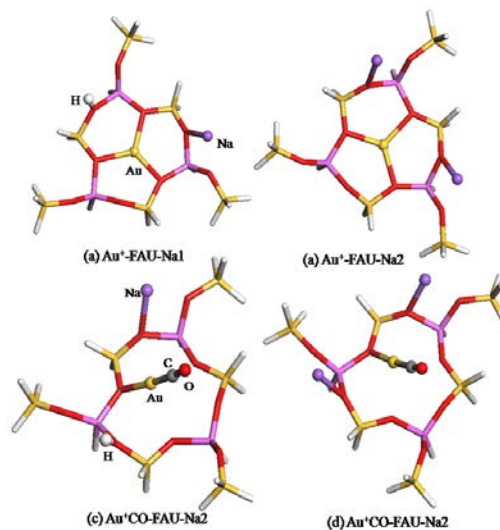


FIGS. 4. OPTIMIZED STRUCTURES OF (a,b) GOLD ATOM (Au⁺) AND (c,d) AND GOLD CARBONYLS ADSORBED ON THE SIX MEMBER RING OF NaY ZEOLITE.

respectively. The CO vibrational frequency in the supported gold carbonyls is markedly different from the gas phase values.This suggests that the zeolite structure has a significant effect on the υ-CO of the supported moiety.Gates and his group, in their experimental study of tricarbonyls of mononuclear gold Au⁰ supported on zeolite NaY using X-ray absorption spectroscopy found three υco bands at 2070, 2033 and 2000 cm⁻¹. Sterrer et. al. in their investigation of CO adsorption on Au/MgO involving a single gold atom using EPR and STM found red shifts in the CO vibrational frequency of 290 and 220 cm⁻¹ by using perfect MgO(100) and O-deficient MgO samples, respectively.A DFT based theoretical investigation by Castellani and co-workers regarding interaction of CO on gold atoms adsorbed on anionic (O²⁻) and neutral oxygen vacancy (Fs) sites of MgO(100) surface revealed red shifts in the CO vibrational frequency between 232 and 358 cm⁻¹ over that of free CO. For the supported gold carbonyl in the neutral state, the electron cloud is relatively more polarizable than that in the other cases because the nearest neighbor oxygen atoms of the zeolite framework are more distant.As a result, there is a substantial charge transfer to CO, thus populating the 2π* antibonding orbital, which leads to the large red shift in the CO vibrational frequency.

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## Conclusions

The adsorption of the CO molecule has been investigated on the gold monomer in two oxidation states 0 and +1 in the gas phase and on a zeolite support using density functional theory. The results of our study reveal that for the gas phase AuCO, the vibrational frequency of CO is red shifted over that of free CO ($\Delta \upsilon$ = -128.9 and cm$^{-1}$), while in case of Au$^+$CO, it is blue shifted ($\Delta \upsilon$ =83.7 cm$^{-1}$). For the supported monomer, the Au-O bond lengths are shorter in case

of carbonyl complexes. Thus CO facilitates stronger interaction of the gold monomer with the support.For the supported carbonyls, CO vibrational frequencies have the values 1854.2, 1890.9 and 2000.1 cm$^{-1}$ for structures containing one, two and three sodium cations, respectively. For the oxidation state +1, the vibrational frequencies are 2157.2 and 2143.7 cm$^{-1}$, respectively for structures having one and two sodium cations. Thus the vibrational frequencies increase on going to higher oxidation states.

TABLE 2. COMPUTATIONAL RESULTS OF NaY ZEOLITE SUPPORTED au ATOM: BOND DISTANCES (Å), BOND ANGLES (DEGREE), MULLIKEN CHARGES (q) OF SELECTED ATOMS, VIBRATIONAL FREQUENCY (cm$^{-1}$) AND ADSORPTION ENERGY (eV).

| | Au-FAU-Na1 | Au-CO-FAU-Na1 | Au-FAU-Na2 | Au-CO-FAU-Na2 | Au-FAU-Na3 | Au-CO-FAU-Na3 | Au$^+$-FAU-Na1 | Au$^+$CO-FAU-Na1 | Au$^+$-FAU-Na2 | Au$^+$CO-FAU-Na2 |
|---|---|---|---|---|---|---|---|---|---|---|
| Bond distances | | | | | | | | | | |
| Au-Oz | 2.36 | 2.10 | 2.30 | 2.09 | 2.52 | 2.04 | 2.17 | 2.05 | 2.15 | 2.06 |
| Au-Al | 3.41 | 3.29 | 3.26 | 3.16 | 3.44 | 3.09 | 3.10 | 3.26 | 3.15 | 3.19 |
| Au-Si | 3.23 | 3.05 | 3.26 | 3.12 | 2.95 | 2.89 | 3.11 | 3.12 | 3.10 | 3.15 |
| Au-O$_H$ | 2.91 | 3.14 | 2.97 | 3.57 | | | 3.21 | 3.09 | | |
| H-Oz | 1.02 | 1.02 | 1.06 | 1.02 | | | 0.98 | 0.98 | | |
| Na-Oz | 2.22 | 2.29 | 2.27 | 2.25 | 2.22 | 2.20 | 2.18 | 2.19 | 2.15 | 2.15 |
| Au-C | | 1.88 | | 1.87 | | 1.82 | | 1.82 | | 1.82 |
| C-O | | 1.19 | | 1.18 | | 1.17 | | 1.14 | | 1.14 |
| Bond Angle | | | | | | | | | | |
| Au-C-O | | 142.1 | | 149.5 | | 178.6 | | 175.7 | | 175.6 |
| Charges | | | | | | | | | | |
| q( Oz) | -0.63 | -0.65 | -0.65 | -0.65 | -0.59 | | -1.35 | -1.33 | -1.34 | -1.33 |
| q(Au) | 0.41 | 0.38 | 0.38 | 0.30 | 0.35 | | 0.77 | 0.71 | 0.76 | 0.72 |
| q(Na) | 0.48 | 0.48 | 0.48 | 0.48 | 0.47 | | 0.98 | 0.98 | 0.98 | 0.98 |
| q(C) | | 0.24 | | 0.25 | | | | 0.44 | | 0.43 |
| q(O) | | -0.11 | | -0.12 | | | | -0.36 | | -0.37 |
| $\Delta q$ | | | | | | | | | | |
| Vibrational Freq | | | | | | | | | | |
| $\upsilon$-CO | | 1854.2 | | 1890.9 | | 2000.1 | | 2157.2 | | 2143.70 |
| Binding Energy | | | | | | | | | | |
| $\Delta E$-Au (eV) | 0.43 | | -0.66 | | 0.49 | | 11.64 | | 10.61 | |
| $\Delta E$-CO (eV) | | 1.19 | | 1.21 | | 0.53 | | -36.12 | | 1.16 |

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